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The Zone-Refining of Aluminum with Copper as the Major Impurity

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THE ZONE-REFINING OF ALUMINUM AND MAGNESIUM
WITH COPPER AS THE MAJOR IMPURITY

A Thesis

Presented to

the Faculty of the Department of Metallurgy
Montana School of Mines

In Partial Fulfillment
of the Requirements for the Degree
Bachelor of Science in Metallurgical
Engineering

by

Arlan Edward Rathke

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CHAPTER I

Introduction and Problem

Eight years ago a new technique which is rapidly proving to be a valuable and versatile tool to the metallurgist was discovered. This simple process, called "zone-refining", is capable of producing certain materials with a degree of purity which has never before been achieved. Although most of the applications of zone-refining have been in the field of research, ultra-pure germanium for use in transistors and rectifiers is being produced on a commercial scale.

The process of zone-refining utilizes the principle that impurities are not equally soluble in the liquid and solid phases of the parent material. This principle is illustrated in the age-old process of producing applejack.¹ The keg of fermented cider is allowed to freeze--the water freezing to the outside with the alcohol (the impurity) being forced to the inside where it can be drawn off in concentrated form.

Zone-refining of materials is just as simple. A bar of impure material is slowly passed through an induction coil which produces an electric field to melt that length of the bar within the coil. As the bar proceeds through the coil, the molten zone moves along the bar picking up and holding the impurities in the liquid phase, Fig. 1. The impurities are held in the liquid phase until the end of the

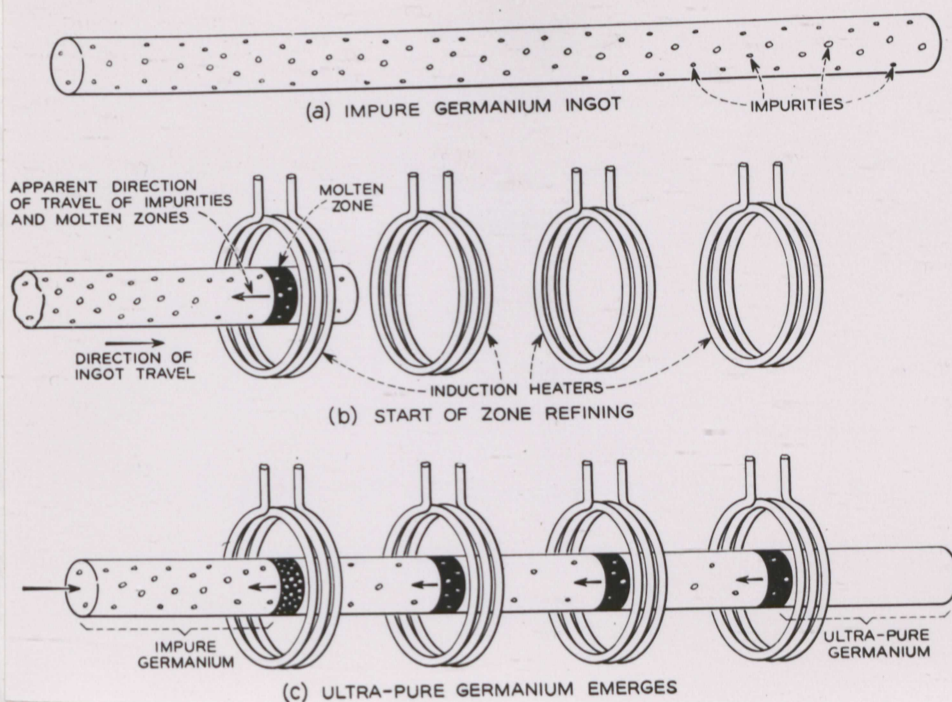


Fig. 1—Zone-refining technique. As the molten zones travel through the ingot, each carries a fraction of the impurities toward the end of the ingot, leaving purified material in the remainder.

(Pfann - Bell Laboratory Record)

bar is reached where the impurities freeze out. This produces a bar which is of extreme purity at one end with a build up of impurity at the other end. The degree of purity produced by the process depends upon the number of passes, the initial impurity level, the difference in solubility of the impurities in the liquid and solid phases, and the length of the molten zone.

For some time zone-refining was used only to produce ultra pure rarer metals such as germanium and titanium; however, with the realization that zone-refining might be used to study the effects of trace impurities upon the physical properties of the common metals, work was begun on copper, lead, and others.

Problem

The purpose of this paper is to report on the investigation of the possibility of removing impurities from the two important light metals, aluminum and magnesium, by applying the principles of zone-refining. The impurities in these metals are namely iron, silicon, and copper, which is the main impurity. Copper and iron come from the reduction cells, while silicon is introduced during the preparation of the material for the reduction bath.

CHAPTER II

Review of Literature

The process of zone-refining, first reported in the literature in 1952², is one part of a vast new metallurgical field called zone melting. This field contains such processes³ as zone leveling, temperature gradient melting, zone remelting and levitation melting. These processes of zone melting have given to the metallurgist a powerful tool for the manipulation of the impurities in metals. Since the discovery, studies have been made on the effect of zone melting processes on a few binary alloy systems.

W.G. Pfann of the Bell Telephone Laboratories is credited with the discovery of the principles of the zone-refining process². The first application was in the production of ultra-pure germanium for use in transistors. The production of germanium and silicon transistor material is the only commercial usage of zone-refining at present; however, much zone-refining is being done on a small laboratory scale. The germanium produced is probably the purest metal known to man with the concentration of impurities throughout most of the ingot being less than 1 part in 10,000,000 parts of germanium⁵. The germanium ingot can be converted from a polycrystalline material to a single crystal is placed at the leading end of the ingot.

In order to provide the desired level of electrical conductivity in the transistor material, Pfann and Olsen⁵ have made use of another zone melting technique, zone leveling. In zone leveling a small amount of impurity, such as antimony in the case of germanium transistors, is placed in a groove at one end of the ingot. The amount of impurity needed to produce the desired electrical conductivity is 1 part of impurity to 100,000,000 parts of germanium⁵. As the molten zone is moved down the ingot, there freezes out behind a solid in which the antimony concentration is proportional to that in the zone. Little antimony is lost from the zone, therefore, the antimony concentration in the zone and in the solid freezing behind the zone remain essentially constant⁵.

Zone-refining has been successfully used to remove lead impurity from gallium by Detwiler and Fox⁶. They were forced to place cooling coils between the induction coils to maintain several separate molten zones within the ingot. The need for the cooling coils was caused by the low melting temperature and high thermal conductivity of gallium.

Tanenbaum, Goss, and Pfann have zone-refined antimony and tin by using a reciprocating method of passing the zones through a straight ingot⁷. The reciprocating heater method may be described as follows: the stroke length is equal to the distance d between the induction coil heaters. "A stroke

begins with the leading edge of the ingot about to emerge from the first heater. The ingot is slowly advanced a distance d , whereupon it is rapidly returned to its starting position, transferring each molten zone to the next heater. Repetitions of this cycle can effect the passage of any number of molten zones through the ingot⁷. The main advantage of the method is the savings in time and apparatus.

The impurities in the antimony--nickel, arsenic, lead, silver and copper--were concentrated in the expected manner with the exception of arsenic which has an equilibrium distribution constant close to one. Lead, copper, and iron were the impurities moved in the tin.

During the refining a nitrogen atmosphere was used for antimony and a vacuum for tin.

The elimination of bismuth impurity from lead by zone-refining was investigated by Westerman⁸, but only fair results were obtained.

Tolmie and Robins⁹ have applied the principles of zone-refining to copper. The impurities investigated were chromium, cobalt, iron, nickel, silver, antimony, manganese, silicon and tin. The experiment, performed under a hydrogen atmosphere, showed the effects of zone speed and number of passes upon the concentration of the impurities. The work also showed that the phase diagrams of copper binary systems could be used to estimate the segregation charac-

teristics of alloying elements during zone-refining. The results obtained experimentally were in approximate agreement with the calculated values.

Researchers at Westinghouse¹⁰ have applied the zone-refining technique to titanium and silicon which are so active that they react with any type of crucible. The process, called cage refining, is carried out in a low pressure helium or argon atmosphere. The center of a fluted ingot is melted by induction while the outside surface remains solid. By passing the ingot through the heating zone, impurities with a preference for the liquid state are collected in the liquid core and moved to one end of the ingot. Thus the ingot acts as its own crucible. Metal produced by this process possesses a purity comparable to zone-refined germanium. Cage-refining may be the future method of purifying highly active metals.

Because the original method was time consuming, Pfann has proposed a system of continuous zone-refining³. In continuous zone-refining, impure material continuously enters at the midpoint of a column through which molten zones are traveling. The pure product leaves at one end while impure waste leaves at the other end. This process produces a relatively large amount of purified material per unit of time.

Another development by Pfann in the field of zone melting is his concept of temperature gradient zone melting¹¹.

A feature of this technique, which requires no movement of material or zones, is that molten zones of very small dimensions can be caused to move about in a solid crystal. For example, a thin sheet of aluminum can be made to migrate through a slab of silicon by applying a temperature gradient perpendicular to the aluminum sheet. The molten aluminum layer moves by the following method³. When the aluminum sheet is heated, a low melting alloy is formed by dissolving silicon. Because of the temperature gradient, one interface of the aluminum layer is hotter than the other. This means that more silicon will dissolve at the hotter point. This in turn sets up a concentration gradient of silicon across the layer, causing silicon to diffuse from the hot interface to the cooler interface at which it freezes. The temperature gradient method is used at present to produce semiconductor devices.

The newest branch of zone melting is levitation melting which was discovered during zone-refining research. The technique, discovered by Westinghouse researchers, is being used to produce highly purified ingots of extremely active metals on a laboratory scale. In levitation melting compressed metal powder is placed inside a high frequency induction coil. The electric current flowing through the coil not only melts the metal but also creates a field of force which floats the metal within the coil. This simple

process, which is carried out in an inert atmosphere, is rapidly proving to be an excellent means to melt and to purify the active metals.

Although the field of zone melting is relatively new, it may no longer be considered a laboratory curiosity. In only a matter of time the methods of zone melting will be used on a commercial basis. Until that time the principles of zone melting can be used to further the knowledge of the basic mechanisms of physical and process metallurgy.

CHAPTER III

General Theory

If a charge of binary solid-solution alloy is melted and then frozen slowly from one end, as for example in one method of making single crystals, coring usually occurs, with a resulting end-to-end variation in concentration. Such coring, or normal segregation, is undesirable where uniformity is an object. For certain systems, coring can be utilized to refine a material by concentrating impurities at one end of the ingot².

An alloy of two elements, in which there is formed a continuous range of solid-solutions, usually does not melt as a simple compound. A temperature is reached where the solid-solution is in heterogeneous phase equilibrium with a liquid solution of different composition. The temperature dependence of these equilibrium compositions is indicated by the phase diagram. For very small concentrations of a solute B in a solvent A, this usually takes the form of Fig. 2¹².

Zone melting is a particular process in which separation of impurities is effected by slowly moving a narrow melted zone through a bar of solid material. Separation occurs if the solid, freezing from a solution at any moment, has a composition different from that of the liquid from which it is freezing¹³.

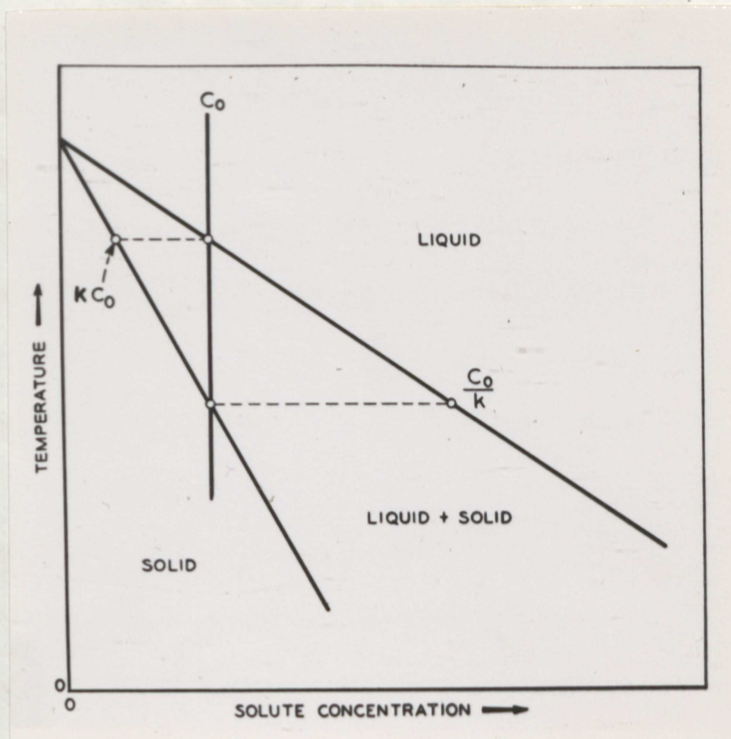


Fig. 2. Schematic phase diagram of conditions favorable to zone-refining.

A number of simplifying assumptions are invoked which provide a suitable point of departure for more refined treatments. These assumptions are as follows: (1) uniform composition in the liquid, (2) negligible diffusion in the solid, (3) a constant distribution coefficient, k , (4) constant length of the liquid zone (except at the ends), and (5) solubility of the solute in the melt is not exceeded at any point¹³.

After repeated unidirectional passage of a molten zone through a bar of material, impurities are concentrated in the ends of the bar. A limiting concentration gradient is reached in the bar after a large number of passes of the molten zone. Both the magnitude of this limiting concentration gradient and the rate of movement of solute in any pass depend on the zone length and on the equilibrium concentrations of solute in the liquid and solid phases. The basic feature of the zone melting process, that is, the attainment of a limiting composition, is relatively independent of the previously stated assumptions².

Path of Impurities

Solutes which lower the freezing point tend to remain in solution and are moved in the direction of zone travel. Solutes which raise the freezing point will preferentially freeze out, and they are moved in a direction opposite to that of zone travel¹³.

When the constant distribution coefficient is greater than one, any atom of solute cannot move in one pass a distance greater than the zone length. As the movement of the solute becomes greater, the number of passes required to give the limiting concentration gradient decreases.

The shorter the zone length, the steeper is the concentration gradient, which results for the limiting distribution. The use of a relatively long zone length in the initial passes causes a rapid movement of solute, while a short zone length in the later passes promotes greater purification from the solute¹³.

By inspecting a phase diagram the path of the impurity is determined. If the solidus and liquidus slope upward, k is greater than 1. Conversely, if the solidus and liquidus slope downward, k is less than 1, and the approximate value of k is calculated from the phase diagram.

Reiss has formulated several qualitative features related to the efficiency of zone-refining. For small values of k , the solute has a large drift velocity and is swept out of the initial zone of the bar more rapidly. Hence small values of k produce large refining efficiencies. If the zone is large, the solute can diffuse back to the initial zone of the bar so as to neutralize the effects of small values of k .

Mathematics of Zone Refining

Much work has been completed in mathematically analyzing zone-refining, which makes it possible to predict the approximate number of passes necessary to remove the solute to a given percentage. Phann has indicated an approximate method for computing the solute-distribution curve in a zone-melting process after an arbitrary number of zone passes are completed for a particular value of the segregation constant which is later defined. Only the practical points of the theoretical mathematics will be reviewed because a complete mathematical analysis is beyond the scope of this text.

The distribution coefficient, k , is defined as the ratio of the impurity concentration in the solid ingot at a distance x from the end of the bar during the n th passing of a molten zone to the impurity concentration of the liquid zone from which the solid at distance x is formed at equilibrium¹².

If a molten zone of length L is allowed to traverse a charge of composition C_0 , the course of segregation during this process may be visualized. As the molten zone advances, it freezes out a layer dx of solid and melts a layer dx of charge. The first solid to freeze at $x = 0$, is of concentration kC_0 . For k less than 1, kC_0 is less than C_0 and hence the liquid is enriched in solute. As the zone progresses, the liquid continues to be enriched, although at

a decreasing rate, until a concentration of C_0/k is attained. When this condition is reached, the concentration of solids entering and leaving the zone are the same and hence no further change of concentration occurs in the zone or in the solid freezing from it until the zone reaches the end of the charge. The remaining liquid then solidifies by normal freezing. Thus as shown in Fig. 3, simple zone melting of a uniform charge results in an initial transition region; a region of uniform concentration which may have any desired length, and an end region of length equal to one zone, in which normal freezing occurs. The concentration C at any distance x in the zone-melted bar (except in the last zone) is given by the following equation²,

$$C/C_0 = 1 - (1 - k)e^{-kx/L}.$$

From Fig. 2 it is seen that repeated passages of the zone will eventually eliminate the plateau of the curve and a definite concentration gradient is established.

Ultimate Distribution

After repeated passes in one direction a distribution is reached which cannot be further changed. (The effect is like piling a given amount of sand against a vertical wall, there is a maximum attainable height.) Pfann calculated ultimate distributions for small values of k around 0.1 and found the ultimate concentration at $x = 0$ is less than C_0 .

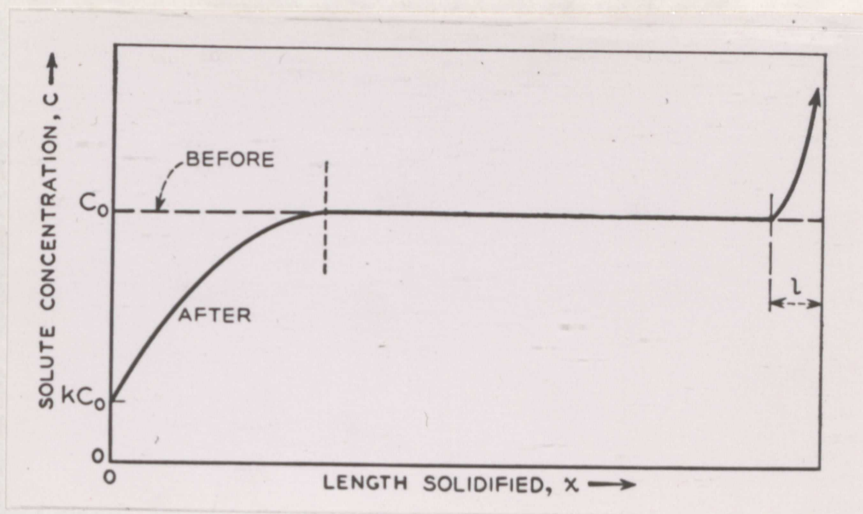


Fig. 3. Approximate concentrations before and after single-pass zone-melting. Note region of uniform concentration after zone-melting.

by a factor of 10^{14} .

Since the concentration at the starting end is decreased by a factor of the order of k in each pass, at least 14 passes^2 are required to approach the ultimate distribution.

Consideration of Systems

In both the Al-Cu and the Mg-Cu systems, Fig. 4, the addition of copper lowers the melting point of the solid solution, but the degree of temperature decrease is small, being approximately 100° for a 5 per cent Cu alloy. Theoretically in both systems the copper should remain in the molten zone and traverse the length of the bar, freezing out in the final zone.

The distribution coefficient k for the Al-Cu system is 0.2 while for the Mg-Cu system it is 0.05. These low k values indicate, according to Reiss as previously stated, that the copper should be swept rapidly from the initial zone of the bar giving a large refining efficiency.

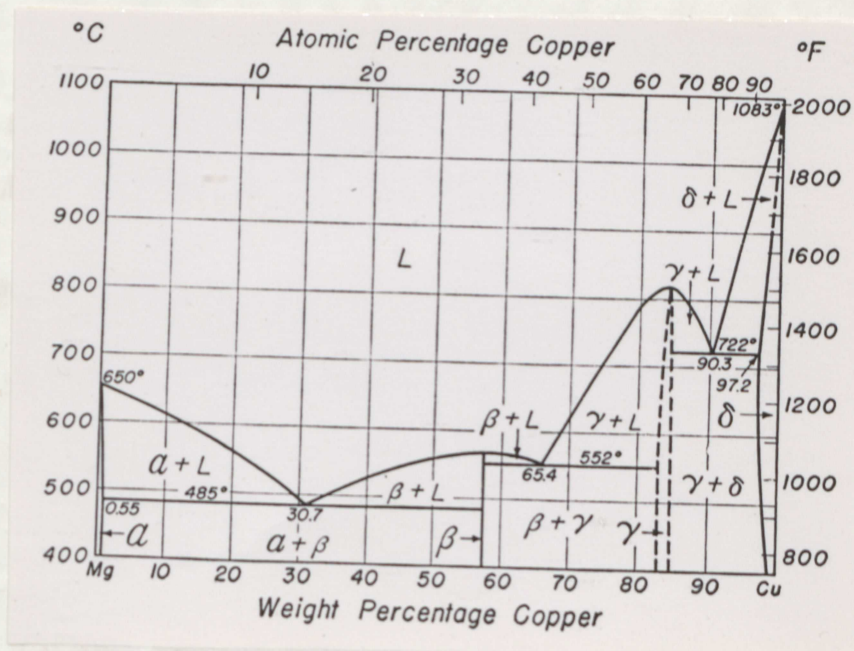
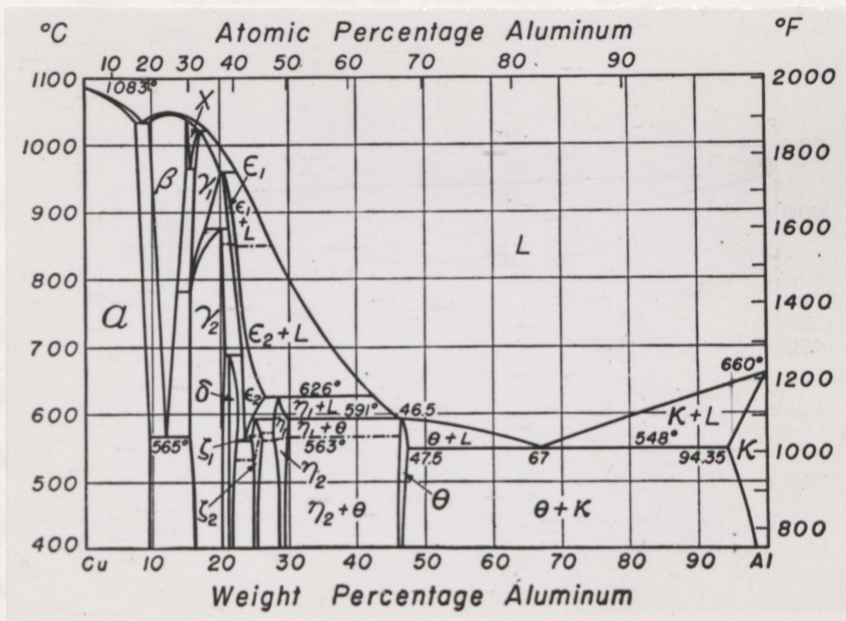


Fig. 4. From ASM Metals Handbook, 1948.

CHAPTER IV

Materials and Methods

A square ingot of the copper-contaminated metal, placed upright in a fired ceramic pedestal, was set in the zone-refining furnace. The molten zone was produced by a moveable high-frequency induction coil, and was intended to carry the copper impurity to that part of the bar which solidified last. After the zone-refining procedure had been completed, the ingot was cut into segments, and analyzed for copper content by the dithizone colorimetric method.

MATERIALS

Aluminum

The aluminum used for the alloy was Hoopes refined metal with a purity of 99.996 per cent.

Magnesium

The magnesium used for the alloy was commercially pure ingot metal with an unknown analysis.

Copper

The copper used for the impurity in the alloys was oxygen free, high conductivity copper.

Pedestal Material

The supports for the metal bars were made from a blend of Tertiary lake bed clays with a small amount of fire clay added. The moistened material was formed by hand into the desired shape. The pedestals (Fig. 5) were fired at 2000F using a heating rate of 300F/hr. The resulting product was smooth and extremely hard. The dimensions of the finished pedestals are; 2 cm dia, and 14 cm length. A square hole $\frac{1}{2}$ cm in cross section was centered in the top of the pedestal.

APPARATUS

Induction Converter

An Ajax Electrothermic Company 3-KVA high-frequency induction converter supplied the power to the induction coil. This converter, a spark-gap type unit, requires about 30 amps and 240 volts to develop maximum power. The condenser and spark-gap are water-cooled requiring a flow of 2 qts. per minute for adequate protection against heat. The converter, shown in Fig. 6 with the complete zone-refining system, has a spark-gap adjustment for roughly controlling the amount of power fed to the coil.

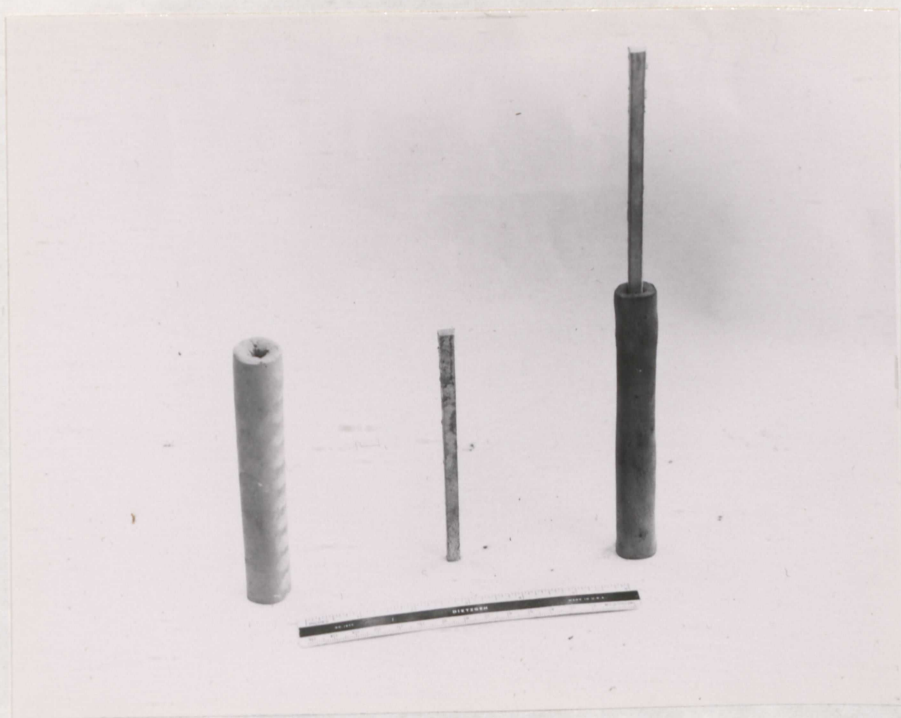


Fig. 5. The pedestal, metal bar, and assemblage.

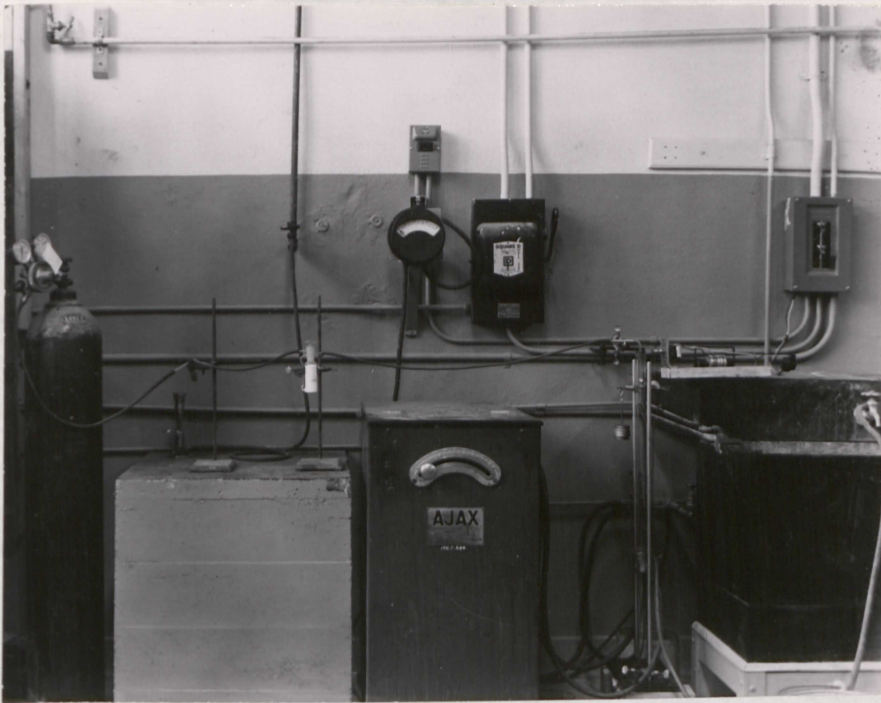


Fig. 6. An over-all view of the equipment.

Casting Furnace

An Ajax Induction Furnace (Fig. 7) with a graphite crucible was used to melt the alloying materials. The induction coils were cooled by water flowing at the rate of 600 ml/min.

Molds

A total of three molds were made from graphite block. The first mold (Fig. 8) had the outside dimensions of $7.6 \times 7.6 \times 12$ cm. The block was cut in half and a $\frac{1}{4}$ in. square hole was cut the entire length of the block with a keyway cutter. The second mold (Fig. 8) had the outside dimensions of $7.6 \times 7.6 \times 16.5$ cm. The block was cut in half, the halves were clamped together, and three $\frac{3}{8}$ in. dia holes were drilled to a depth of 14 cm. Three 1 in. holes were drilled on the opposite side of the block to a depth of 2 cm and connected to the $\frac{3}{8}$ in. holes with $\frac{3}{16}$ in. holes. The third mold (Fig. 8) was cut into one of the halves of the second mold. Two $\frac{1}{4}$ in. square holes were cut straight through the entire length of the block with a keyway cutter. The halves of the mold were held together with clamps during casting.

Zone-Refining Furnace

The furnace (Fig. 9) used for the zone-refining operation was built by the authors, utilizing their own plans

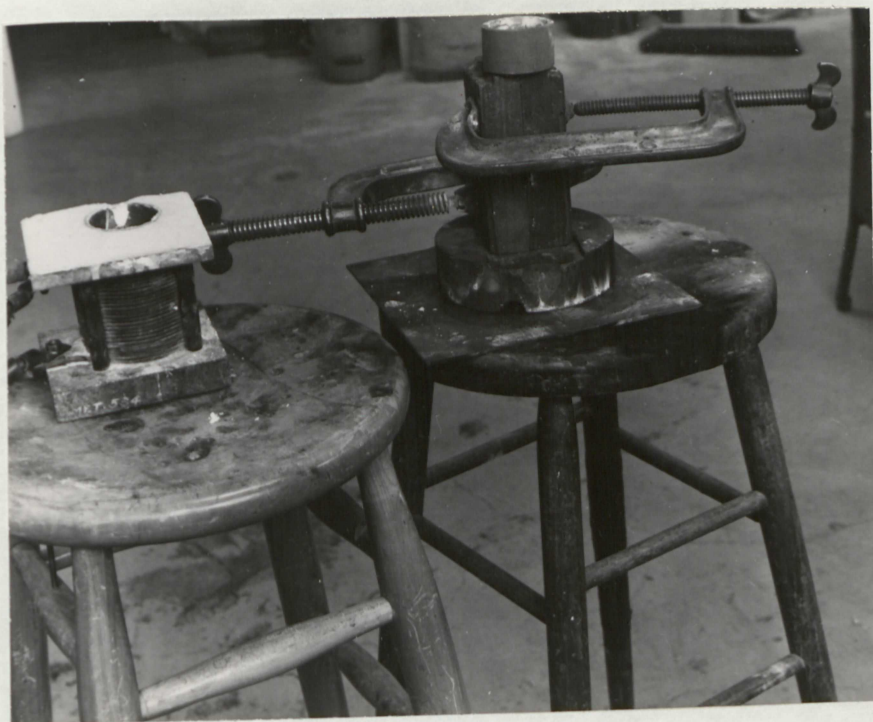


Fig. 7. The bar casting apparatus.



Fig. 8. Left - The first square mold.
Center - The cylindrical mold.
Right - The mold used.



Fig. 9. The zone-refining furnace.

and ideas. A vertical design was followed in building the furnace. A cast iron ring stand with a 3 ft rod was the basis for the construction. To this, another 3 ft rod was added directly in line with the first rod and spaced 8 1/4 in. away. A Vycor high temperature glass tube (1 in. ID) was centered on the ring stand and held in place by means of clamps attached to the 3 ft rods. A hole was drilled in the base to provide a means for the escape of the inert gas which is used in the furnace.

Induction Coils

Two induction coils were made by the authors. The first coil (Fig. 10) was constructed using 3/16 in. copper tubing. The tubing was bent into three loops having a inside diameter of 34 mm. Each loop was insulated from the other with mica and duPont Duco cement. The length of the finished coil was 15 mm. In order to connect the leads from the convertor to the coil, it was necessary to make two connector blocks from electrolytic copper cylinders. These cylinders were turned down on a lathe and threaded to provide a secure convertor connection. One assembly was soldered to each end of the coil.

Because this coil caused the convertor unit to over-heat during zone-refining, a second coil was constructed with more turns so that the impedance of the coil would be more nearly that of the convertor. In order to hold

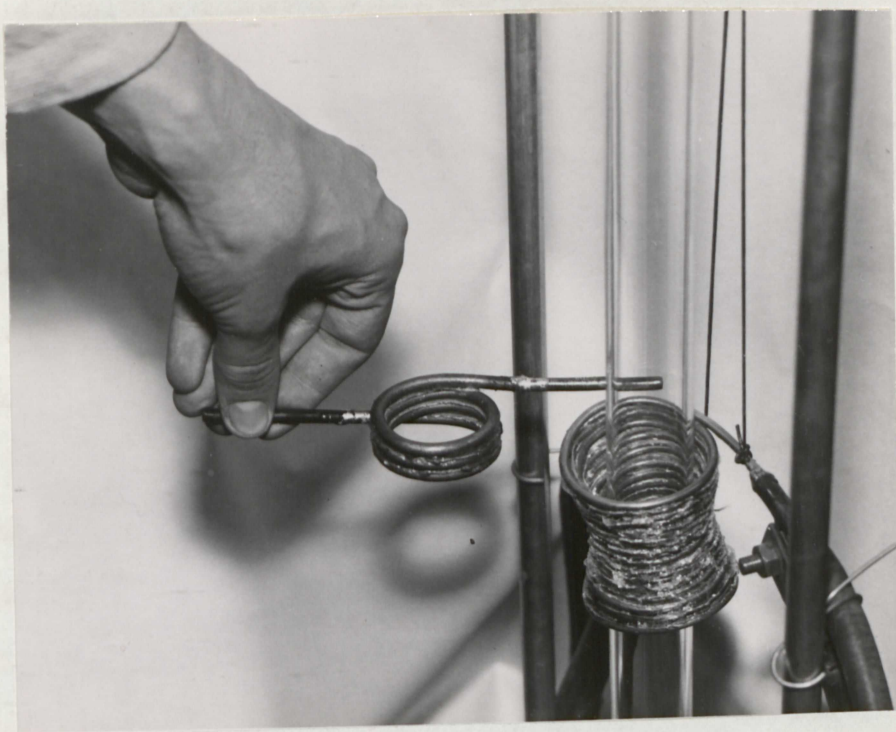


Fig. 10. Left(first coil); Right(present coil).

the zone length to 15 mm and yet produce the needed impedance, the second coil (Fig. 10) was made in a helix shape. A total of 16 turns of 1/8 in. copper tube were formed with the diameter ranging from 55 mm at the top and bottom to 34 mm at the zone. The turns were insulated from each other with mica and duPont Duco cement. The convertor connections from the first coil were removed and soldered to the second coil after adjustments had been made to assure a tight fit.

Although the second coil had more turns than the first, it was discovered by experimentation that only 15 mm in the center of the coil length served as the zone. Because the ratio of the loop diameter to sample cross section is large, the heating effect produced by loops of diameters greater than 34 mm is not great enough to bring about any noticeable melting of the sample bar.

Both coils were cooled with water flowing at a rate of 600 ml/min.

Inert Atmosphere System

Because aluminum and magnesium are susceptible to oxidation at moderate temperatures, it was decided to hold oxidation to a minimum by injecting an inert gas into the zone-refining furnace. The inert gas used was helium. The entire gas system (Fig. 11), a low pressure inert gas system, consists of the following parts: 1) a tank of He, 2) a tube

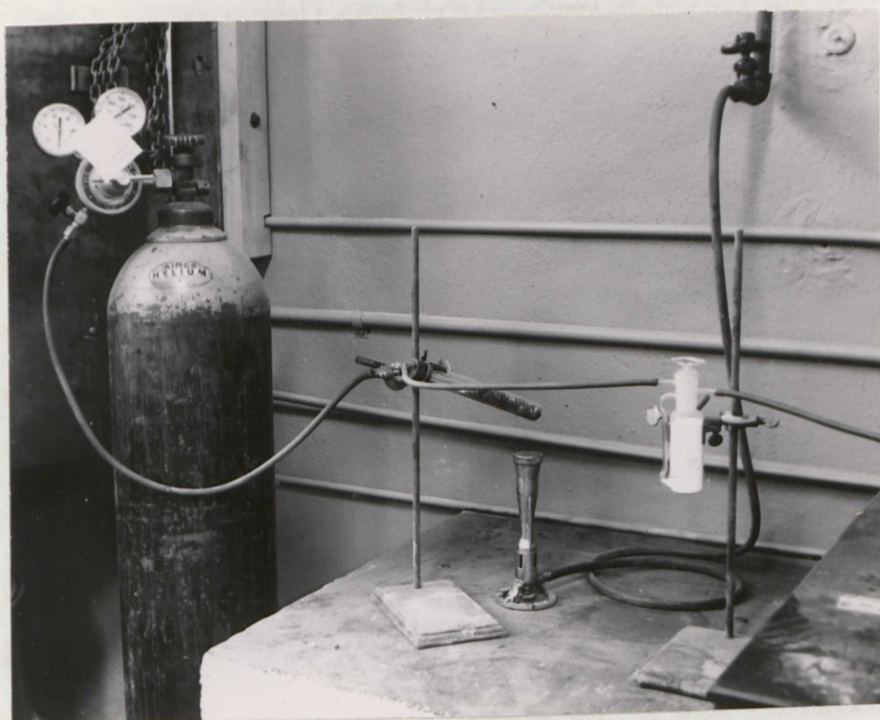


Fig. 11. The inert gas system.

filled with hot copper filings to remove oxygen when hot, 3) a drying unit using calcium chloride as the drying agent, and 4) an inlet to the refining furnace. The helium was forced through the system at a pressure of approximately 1 psig. The used gas was not recycled, but vented to the atmosphere through a hole in the bottom of the cast iron base.

Lowering Mechanism

The lowering of the induction coil over the metal sample was accomplished by the use of a slowly-turning motor. The motor (Fig. 12) used is a 60 cycle Hagen Synchronous Motor with a power rating of 115 volts and 7 watts and a torque of 20 oz-in. The 1/8 in. dia shaft of the motor turned at a rate of 1 rpm. A new shaft, 3/8 in. dia, was made from brass so that Wright & McGill 15 lb. test leader could be wound more easily. The entire motor assembly is attached to a piece of sheet aluminum which in turn is fastened to a piece of wood. The wood piece was placed in position above the refining furnace and fastened to the bench.

A fish hook was attached to the leader and a loop of fish line was fastened to each side of the induction coil. The loop was placed over the fish hook and the line was kept in tension.

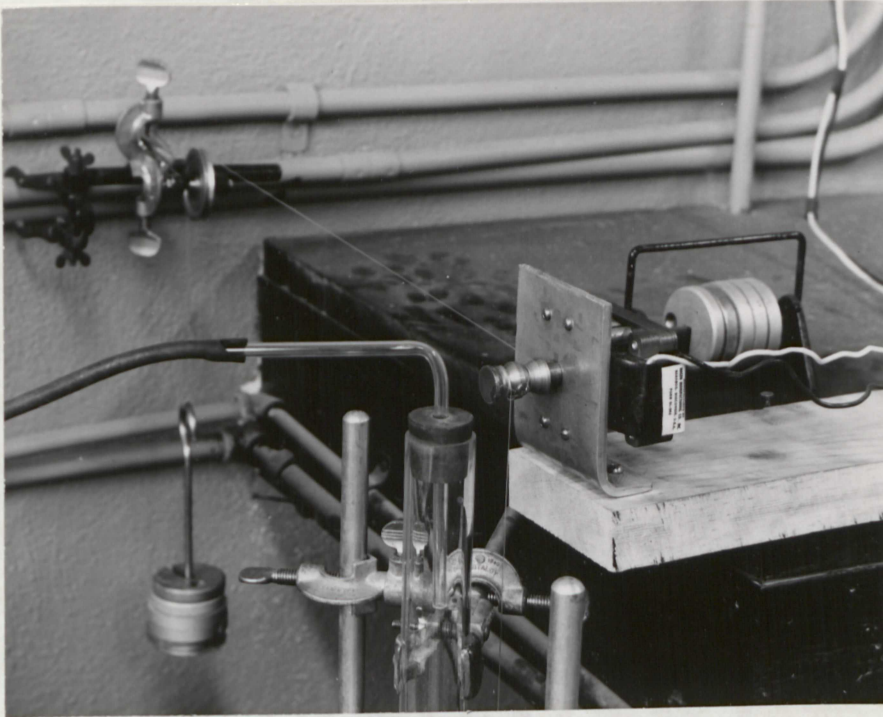


Fig. 12. The lowering mechanism.

The coil was counterbalanced with 500 grams connected to the shaft with fish leader running over a pulley.

Although the above apparatus was extremely crude, it accomplished its purpose of smoothly lowering the coil at a suitable rate.

PRELIMINARY WORK

The Al-Cu and Mg-Cu alloys of 5 per cent Cu content were prepared. A typical charge of approximately 109 g of solvent metal and 5.5 g Cu was melted in the Ajax Induction Furnace. The purpose of using this furnace is two-fold: 1) the speed of melting is rapid, and 2) a mixing action is present.

The molten metal was cast into the mold which was preheated in a pot furnace. The quantity of metal in the bars was approximately 27 g, the remainder being lost as overflow and skull in the crucible.

In the casting of both Al and Mg the temperature control of the furnace was quite important. During the casting of Al the temperature of the molten metal was approximately 700C. This temperature was estimated when the molten metal was gray. Higher temperatures increased the oxidation rate to such an extent that the metal became highly viscous and could not be poured.

The casting temperature of Mg was more critical than the Al because of its highly combustible nature due to

rapid oxidation. Several fires were experienced until the proper technique was developed. The Mg was allowed to melt almost to completion, and a flux of 28% MgF_2 and 72% MgCl_2 ¹⁵ was then added. This flux formed a highly viscous layer over the molten metal, preventing oxidation. To cast the metal the layer of flux was punctured and the metal poured.

The temperature of the furnace was controlled by holding the spark-gap-adjustment at a minimum. Although this increased the time needed for melting the metal, the casting procedure was improved.

Overheating of the mold before casting produced undesirable results. The molten Al would oxidize when coming in contact with the mold, plugging the hole, while the Mg would oxidize and burn. The bars from an overheated mold contained many residual stress cracks.

The preheated mold was set upon a graphite block when casting. Because of overflow during the casting operation, the second hole became plugged. In casting Al the bottoms of the holes were connected and one hole poured. Because of the pressure of the metal and the capillary action involved, the second hole would fill. This did not work for Mg. The Mg probably flowed into the pores of the graphite, which would induce friction and slow up the rate of flow of the metal, causing the metal to freeze before it could rise in the second hole. This conclusion was

drawn from the fact that a thin layer of carbon was imbedded in the surface of the Mg bars. Because the density of Mg is approximately $\frac{2}{3}$ that of Al, the head supplied by the metal was sufficient of Al, but not for Mg.

Because of segregation in the use of the first mold, a condition which was not overcome, and attempt was made to cast alloy bars of circular cross section followed by rolling to reduce the cross section to a $\frac{1}{4}$ in. square. During the rolling procedure many of the residual stresses were propagated into large cracks. Various heat treatments before rolling were attempted to reduce the residual stresses. None of the treatments proved helpful, and the idea was abandoned.

To obtain a greater degree of homogeneity, the bars were heat-treated at 550C in a Lindberg forced air furnace for 4 hr followed by furnace cooling. During the operation the Mg bars ignited. The temperature of the furnace was well below the melting point of Mg, but possibly one or more bars contained small amounts of casting flash which ignited and supplied the necessary heat for combustion of the remaining bars. Because of the size of the bars, they did not have sufficient volume to dissipate the heat and localized hot spots developed.

For the analytical work a 0.001% diphenylthiocarbazone solution was prepared. The trade name of this chemical is Dithizone and this name will be used in future reference.

Five hundredths of a gram of Dithizone was dissolved in 500 ml of CCl_4 . A 50 ml aliquot of this solution was diluted with 450 ml of CCl_4 yielding a solution of 0.001% Dithizone.

ANALYTICAL METHODS

To determine the concentration of the Cu in various sections of the bar, the Dithizone colorimetric method was used. Standard samples containing a known amount of copper in the form of CuCl_2 and Al in the form of AlCl_3 were analyzed and a graph of intensity vs. g of Cu was plotted.

EXPERIMENTAL PROCEDURE

Zone-Refining

The cast alloy bar, 12 cm in length, was first sampled by cutting pieces 0.5 cm in length from each end of the bar. The resulting 11 cm bar was inserted in the hole in the top of a pedestal (Fig. 5), the fit being a force fit. The pedestal and bar assembly was then placed inside the Vycor tube which is clamped into position. The inert gas system is opened and the gas is allowed to flow through the system for 5 minutes during which the system is checked for leaks. Also during the 5 min. period, the water is turned on in the convertor and the coil. The water through the coil is turned on slowly to prevent a sudden buildup of pressure which causes the water tubes to leak. At the end of the

gas flushing period, the coil is located over the top of the bar and the convertor is turned on using a spark-gap-adjustment of 25 degrees left. The coil is left at the top of the bar for 10 min to allow the metal to heat up to temperature and then the lowering mechanism is turned on. The lowering mechanism and the power are turned off when the top of the zone reaches the top of the pedestal. The bars are refined by passing the zone over the bars in multiples of 3 passes before removal from the furnace. Samples for analysis, $\frac{1}{4}$ cm in length, are taken from each end and from the center and the rest of the bar is saved for analysis if required.

Analysis of Refined Bars

The $\frac{1}{4}$ cm samples were placed in 50 ml Erlenmeyer flasks and dissolved by the following method: the samples from the bar were placed in 6 M HCl to bring the Al into solution as a chloride. Nitric acid was added to dissolve the Cu and then the solution was evaporated almost to dryness. Concentrated HCl was added and the solution evaporated almost to dryness. This evaporation process was repeated once more, and the remaining residue dissolved in distilled water. Nitric acid was used because HCl does not dissolve copper. The HCl-evaporation process was used to convert the $\text{Cu}(\text{NO}_3)_2$ to CuCl_2 and rid the solution of nitrate ions, which would have been a source of inter-

ference in the colorimetric determination.

To the solution 1 ml of ammonium citrate was added and two drops of thynol blue indicator was added. The thynol blue turns pink at a pH of 3 and 1 M HCl was added to obtain this acidity. To the solution 2.5 ml of Dithizone was added and the intensity determined by the Coleman Junior Spectrophotometer.

CHAPTER V

Results and Discussion

The results obtained by zone-refining the aluminum-copper alloy bars did not support the conclusion drawn from the phase diagram investigation; however, some factors which may be useful in later work were discovered.

Method

The method used to zone-refine the alloy bars was the cage method suggested by Westinghouse researchers for use on high melting point metals. A review of the published literature shows that this paper is the first application of the cage method of refining metals of lower melting points. Although the induction converter was not particularly suited for this type of experiment, the outer surfaces of the alloy bars radiated enough heat to prevent their collapse during the movement of the zone. However, the power supplied to the induction coil must be rigidly controlled because, if too much heat is induced into the bar, the outer surfaces are not able to radiate the heat sufficiently to prevent the collapse of the metal shell surrounding the molten core. A setting of 25 degrees left on the spark-gap was found to be the maximum power that could be applied without the bar collapsing. For bars of larger cross section, a lower angle setting could be used because

of the greater radiating surface area.

Because of the helix shaped coil a levitation tendency exists at all power settings. The effect upon the bar is greater as the spark-gap angle setting is decreased, i. e., at higher power settings.

Zone Travel

By carrying out the zone-refining operations at night in total darkness, the movement of the molten zone could be observed. During the operation that part of the bar within the coil glowed a dull red. The color was hardly noticeable at the top of the bar becoming more intense as the zone approached the bottom of the bar. Because of the high thermal conductivity of aluminum, the red zone covered a large section of the bar, thus producing a relatively large moving zone. According to Reiss¹⁴ the production of a relatively large zone does not produce suitable conditions for zone-refining bars with a low coefficient of distribution.

Another indication of a molten moving core was a nub of metal issuing from that end of the bar which was placed in the pedestal. This condition appeared on all bars which were refined.

Analytical Results

The Dithizone colorimetric method proved to be simple and rapid with a high degree of reproducibility. No trouble

was encountered because the standards were made from the same materials as used in the actual experiment, and hence in the standardizing solutions.

Impurity Concentration

Of the seven bars initially scheduled to be refined, only three were analyzed for copper concentration. The other four bars were discarded because of levitation during the procedure. The following remarks and interpretations on the movement of the copper are based upon the assumption that the initial bars were of homogeneous composition with exceptions noted.

Bar no. 1 was subjected to 3 passes of the zone and analyzed. The copper content reported is based upon a 0.5 g sample. The original analysis revealed that the bar was homogeneous (top section vs. bottom section). The analysis of the zone-refined bar disclosed more copper in both the top and bottom sections than existed in the original bar. The results given by the top, middle, and bottom analysis gave no indication of purification. The analysis of the section containing the nob showed a high concentration of copper. This would indicate a movement of Cu with the zone to the end of the bar according to theoretical considerations. Considering the over all analysis of the bar, the copper migrated from the starting end to the nob. The increase in copper concentration in the starting end may

be caused by the relatively large length of the zone, which, according to Reiss¹⁴, would cause the copper to migrate first to the front of the zone and then diffuse back through the zone. This condition may have been brought about during the preheat period.

Bar No.	Section	$\frac{\text{g of Cu}}{.5 \text{ g sample}}$ As cast	No. of Passes	$\frac{\text{g of Cu}}{.5 \text{ g sample}}$
1	Top	0.0145	3	0.0186
1	Center		3	0.0172
1	Bottom	0.01425	3	0.0163
1	Bottom*		3	0.0285
5	Top	0.01708	6	-----
5	Center		6	0.0183
5	Bottom	0.01820	6	0.0164
6	Top	0.01888	9	0.0157
6	Center		9	0.0218
6	Bottom	0.02880	9	0.0296

Table 1. Impurity distribution in a bar.

The top analysis of bar no. 5 (refined) was lost. Therefore, no definite conclusions can be drawn from the data.

Bar no. 6, which was subjected to 9 passes of the zone, showed a definite tendency toward movement of the copper impurity with the zone. The initial zone of the bar was decreased in copper content to a sufficient degree while the middle showed an increase in copper content with a slight increase in the bottom section.

As stated before, the above statements were made on the basic assumption that bars were homogeneous; however, actual analyses of the bars showed that they were far from homogenous. Therefore, at this time no definite conclusion can be reached on the effect of the zone-refining principle when applied to aluminum with copper impurity.

CHAPTER VI

Summary and Conclusion

Although zone-melting is not being used on a large scale commercially, it is rapidly becoming a basic tool in research. With the increasing need for ultra-pure metals in many applications, only a period of time exists before zone-refining becomes a common metallurgical process with wide industrial usage. Until such a time zone-melting will continue to be studied in the laboratory in search of many new applications.

This thesis presents the first known application of cage-refining as applied to a light metal with a relatively low melting point. Despite the crudeness of the apparatus some definite conclusions can be drawn concerning the application of cage-refining to aluminum with copper impurity.

The following conclusions have been drawn:

1. Aluminum will serve as its own crucible during cage-refining if the temperature is controlled.
2. Zone-refining may be accomplished by using a moving coil to induce the molten zone with a stationary metal sample.
3. Within the limits of experimental error copper will move in aluminum in accordance to phase diagram predictions.

Since the field of zone-melting is relatively new, much work remains to be accomplished. Further work on the alloy system of aluminum will prove beneficial both to the student and to future metallurgical progress.

CHAPTER VII

Recommendations

From the data obtained during this experiment there is obviously much room for improvement. The following recommendations are made:

1. A new convertor unit with an adjustable impedance would be advisable. This would allow the use of a small coil and a small effective zone.
2. Because a synchronous motor was used, a variac could not be used to regulate the speed of the motor. The construction of a gear box for speed variation would be desirable. This would allow a study of the effect of impurity movement with varied drop rates.
3. A coil of approximately one turn would be advantageous in future work on aluminum. This would yield a highly effective movement of copper.
4. In the heat-treating of Mg it is advisable to use a temperature of 400-450C rather than the 550C which was used. The bars should be cleaned of any small chips for it is believed that it was small pieces of casting flash which first ignited and supplied the necessary heat for the combustion. The size of the bar is also a major factor for a large bar will radiate the heat faster than a

small bar which will prevent localized heating.

5. An attempt should be made to secure commercial alloy bars cut to size. These bars may contain other alloying elements, besides the designated impurity, which could be studied. The acquisition of these bars would eliminate the casting procedure.
6. Some attempt should be made to analyze the bars in a non-destructive manner before zone-refining. In this way a better knowledge of impurity movement will be gained.
7. For better temperature control a means of measuring the temperature of the bar should be devised.
8. An investigation into the use of coiling coils to combat the high thermal conductivity of the aluminum should be made.
9. The horizontal method of zone-refining should be tried on the Al-Cu alloy to determine if the impurity actually moves.

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process, which is carried out in an inert atmosphere, is rapidly proving to be an excellent means to melt and to purify the active metals.

Although the field of zone melting is relatively new, it may no longer be considered a laboratory curiosity. In only a matter of time the methods of zone melting will be used on a commercial basis. Until that time the principles of zone melting can be used to further the knowledge of the basic mechanisms of physical and process metallurgy.